Cathodic Synthesis of Unsymmetrical Diphenylhydrazine

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The electro chemical reduction of N,N-diphenylnitrosamine in alcoholic medium using hydrochloric acid as supporting electrolyte have been studied in detail. The effect of catholyte composition, temperature and cathode material have been invest-igated to optimise the yield of the reduced product, N.N-diphenylhydrazine. The polarization studies were made to choose suitable current density for the reduction. A plausible mechanism of the reduction has been proposed.

The unsymmetrical hydrazines have been the subject of extensive investigations world over because of their use as propellant in rockets. They have been prepared by conventional chemical[2-5] and electrochemical methods. The electrolytic preparation of unsymmetrical dimethylhydrazine was first reported by W.G. France and co-workers[6,7]. Lund[8] and others[9] studied their behaviour on dme in aqueous sulphuric acid. Russian authors[10] have also studied the electrolytic preparation of unsymmetrical dialkylhydrazine in mineral acid using high hydrogen over-voltage metals like lead. Udupa and co-workers[11] using rotating Pb and Cu cathodes have reported the optimum conditions for the preparation of unsymmertical dimethylhydrazine in aqueous medium using sulphuric acid as supporting electrolyte.

A survey of the literature reveals conventional chemical preparation of N,N-diphenylhydrazine by the reduction of diphenyl nitrosamine using zinc and acetic acid in ethanolic medium[12]. The procedure seems to be uneconomical as it involves the use of costly metal zinc and imposes serious separation and pollution problem. There has been no report however, on the comparatively better electrolytic method of preparation of the compound so far. In view of the above we undertook a detailed investigation to find out the optimum conditions for the electrolytic reduction of N,N-diphenylnitrosamine to unsymmetrical diphenylhydrazine in alcoholic (ethanol and methanol) medium using hydrochloric acid as supporting electrolyte and source of proton. The effect of temperature, cathode material and composition of catholyte have been investigated using a divided cell with porous diaphragm.

EXPERIMENTAL

Diphenylamine (BDH) was purified by recrystalization (m.p. 53°C). The corresponding nitroso derivative was prepared by the reported method[12]. HCl used was of laboratory grade. Ethanol and methanol (L.R.) were used after distillation.

CELL ASSEMBLY

A 500 ml beaker with provision to hold cathode, porous diaphragm. thermometer and magnetic stirrer was used as electrolysis cell. Hg, Cu and Pb were used as cathode material and platinum foil inside the diaphragm served as anode in each case. All the experiements were carried out at constant current-0.3 Amp. c.d. (0.0078 Amp/cm^2).

ELECTROLYSIS, WORK UP AND ANALYSIS

Following is the details of the electrolysis.
Catholyte: 100 ml ethanol or methanol, having 5, 10, 15 or 20% HCl (v/v) as supporting electrolyete and 1.0 gram (0.005M) of N.N-diphenylnitrosamine.
Anolyte: 40 ml 10% (v/v) HCl in ethanol or methanol.

After passing the current for the sufficient time corresponding to 4F/mole, the catholyte was filtered off and the solution was evaporated on a water bath to the point of crystallization. After cooling the contents of the flask, blue coloured needles of N,N-diphenylhydrazine hydrochloride separated out. These were filtered and dried at vaccum pump. The m.p. (165-66°C[13]) showed it to be pure N,N-diphenylhydrazine hydrochloride. After keeping the filterate, a further crop of crystals was obtained from the mother liquor. The yield of the product obtained in each experiment has been ascertained (Tables I-IV). The characterization of the product, N,N-diphenylhydrazine hydrochloride, has been done by its elemental analysis (Found C, 65.85; H, 6.00; N, 11.92. $C_{12}H_{13}N_2Cl$ - requires C, 65.30; H, 5.89; N, 12.69%) and I.R. of the authentic sample.

RESULTS AND DISCUSSION

The results obtained indicates that the electrochemical reduction of N,N-diphenylnitrosamine(1) proceeds smoothly at Hg,Cu and Pb cathodes in EtOH, and MeOH, containing 5, 10, 15 or 20% HCl

TABLE 1

EXPERIMENTAL DETAILS OF THE REDUCTION OF N,N-DIPHENYLNITROSAMINE IN ETHANOL, CONTAINING 10% HCl; C.D.0.0078 AMP/CM^2. ANODE PT FOIL; CURRENT 0.3 A

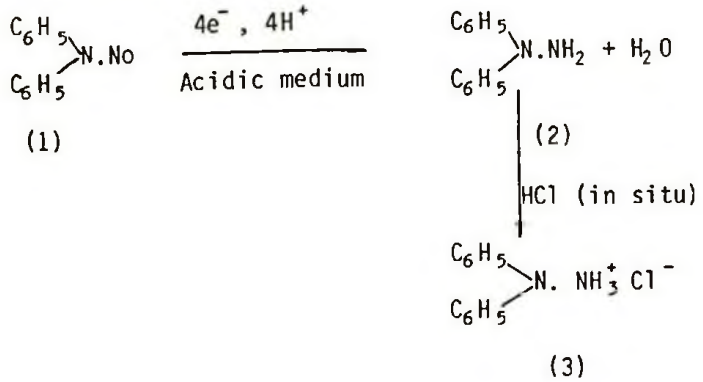
S.N.	Cathode	Cell voltage (V)	Mass yield as Hydrochloride (%)
1.	Hg	5-7	59.1
2.	Cu	9-10	65.5
3.	pb	5	55

TABLE 2

EXPERIMENTAL DETAILS OF THE REDUCTION OF N,N-DIPHENYLNITROSAMINE METHANOL, CONTAINING 10% HCl C.D. 0.0078 AMP/CM^2. ANODE PT FOIL; CURRENT 0.3 A

S.N	Cathode	Cell voltage (V)	Mass yield as hydrochloride (%)
1.	Hg	8	56
2.	Cu	7-9	64
3.	pb	10-12	53.6

as supporting electrolyte and leads to the formation of corresponding hydrazine hydrochloride (3), via hydrazine (2).



(1) (2) (3)

The reduction of N, N-dialkylnitrosamine appear to proceed in the manner as suggested by Nikulin and Klochkova[10]. The organic substrate first undergoes protonation which is followed by one electron-transfer forming the free radical R_2 N.NOH which immediately takes up three more protons and three electrons simultaneously forming the hydrazine.

TABLE 3

EFFECT OF CATHOLYTE CONCENTRATION; CATHODE, Hg POOL; TEMP. 25±2°C; C.D. 0.0078 A/CM^2.

S.N.	Catholyte composition (% HCl V/V in alcohol)	Mass yield as hydrochloride(%)
1.	5	58
2.	10	59.1
3.	15	58.2
4.	20	57.6

TABLE 4

EFFECT OF TEMPERATURE; CATHODE, Hg POOL; C.D. 0.0078 A/CM^2; CATHOLYTE, 10% HCl IN ETHANOL (V/V)

S.N.	Temp. °C.	Mass yield as hydrochlorde (%)
1.	10	58.6
2.	15	59.2
3.	20	59.1
4.	25	59.0
5.	30	58.5
6.	35	58.7
7.	40	56.2
8.	45	51.0
9.	50	42.0

It was observed during the investigation that the catholyte composition, the nature of solvent,viz. EtOH and MeOH and also the nature of cathode material do not play a very significant role in the reduction in acidic conditions. The overall yield of the product was 55 to 65% in each experiment. Temperature was found to affect the yield adversely above 40°C. At higher temperature, hydrogen evolution becomes dominant.

It may be worthwhile to mention that the electrochemical reduction of N,N-diphenylnitrosamine (1) does not take place in aqueous solutions as reported by earlier workers[6-11]. Our attempt to reduce (1) in aqueous mineral acids using different cathodes like Pb, Hg and Cu and at various temperature leads back to the isolation of the starting material. The reason appears to be that while at lower temperature the nitrosamine is not soluble, at higher temperature only hydrogen evolution is observed in aqueous mineral acids. During the present investigations we found that an alcoholic solution containing

hydrochloric acid is ideal for affecting the reduction in a fairly good yield.

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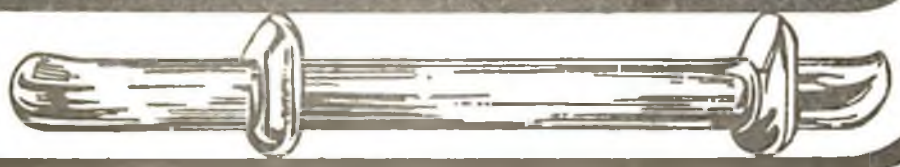
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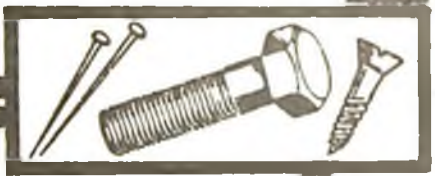
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